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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a block copolymer constituent. In more detail, the block copolymer constituent concerned has the mechanical strength which was excellent while the compatibility of the block copolymer as a constituent and an ester compound was excellent, and this invention relates to the optimal block copolymer constituent for uses, such as a solid electrolyte or a photo-setting resin.

[0002]

[Description of the Prior Art]In order to obtain devices, such as an electrochromic display device, a recording element, a cell, and a sensor, the solid electrolyte prepared by adding and swelling the organic solvent (electrolytic solution) in which metal salt was dissolved to polymer is used. What (M. Watanabe et al., J.Polymer Sci. Polym. Phys., 21,939 (1983)) impregnated with the metal salt electrolysis solution into polar polymers (polyacrylonitrile) concretely as this solid electrolyte, and polar polymers, An electrolytic solution (organic solvent in which metal salt was dissolved), And there are some (KAbraham and M.Alamgir, J.Electrochem. Soc., 137, 1657 (1990)) etc. to which photo-curing of a fixed quantity of ultraviolet rays was irradiated with and carried out to the liquid mixture which consists of a photosensitive cross linking agent.

[0003]On the other hand, the photo-setting resin is used abundantly as a substrate for printing. As this photo-setting resin, epoxy system monomers, such as acrylic system monomers, such as methyl methacrylate, oligomer, or screw FENO Norian A, are concretely used as the main ingredients, and the low-molecular-weight thing of the main ingredients concerned is received, Specified quantity addition of a photopolymerization initiator and the photosensitizer is carried out, respectively, and it constitutes.

[0004]

[Problem(s) to be Solved by the Invention]However, in the conventional solid electrolyte, the

polar polymers themselves plasticized with the electrolytic solution, and there was a problem that the mechanical strength of the polar polymers concerned fell easily substantially.

Therefore, the conventional solid electrolyte was difficult to hold definite shape over a long period of time (gestalt holdout). In the conventional solid electrolyte, since the compatibility of polar polymers and an electrolytic solution was insufficient, when long term storage (storage) was carried out, there was also a problem that an electrolytic solution oozed out easily outside. Polar polymers, such as polyacrylonitrile, had the high melting point, and since it was not processible if it is not under an elevated temperature, they also had the problem that manufacture of the lithium secondary battery etc. which use the polar polymers concerned was difficult.

[0005]On the other hand, in the conventional photo-setting resin, since the monomer and oligomer of low molecular weight were used as the main ingredients, there was a problem that handling was not easy. Then, adding and dealing with a rubber composition and a resinous principle as an amount ingredient of polymers to these monomers and oligomer, and improving a sex is also proposed. However, since an acrylic system monomer and an epoxy system monomer had high polarity, the kind of amount ingredient of polymers to add was limited extremely, or there was a problem that compatibility with the amount ingredient of polymers to add was not enough etc.

[0006]This invention is made in view of an above-mentioned problem, and is a thing. By using the specific block copolymer of \*\*, even if the purpose has the outstanding mechanical strength and is after swelling, it is providing a block copolymer constituent with little aging of shape.

Compatibility with an ester compound is raised, and also when continued and saved at a long period of time (storage), fear of the effusion of the ester compound concerned aims at providing few block copolymer constituents.

[0007]Another purpose of this invention aims at providing the block copolymer constituent which can be manufactured easily.

[0008]

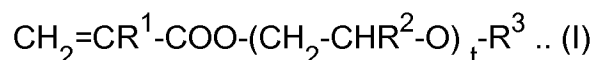
[Means for Solving the Problem]In order to attain the above-mentioned purpose, according to this invention, a block copolymer constituent which makes the following a gist is provided. that is, (1) Make into a constituent at least one polar monomer chosen from a group which consists of the following polar monomer 1, the following polar monomer 2, and the following polar monomer 3. 10-100-mol % -- making the segment A to contain and the polar monomer concerned into a constituent -- less than [ 10 mol % ] -- block copolymer which consists of the segment B to contain, and (2) ester compounds are contained at least.

[0009]\*\* Polar monomer 1 : it is a polar monomer which has at least one sort of functional groups chosen from a group which becomes at least one polymerization nature unsaturated

bond from a hydroxy group, a nitrile group, a carboxyl group, an amino group, and an amide group.

[0010]\*\* Polar monomer 2 : it is a polar monomer expressed with a following general formula (1).

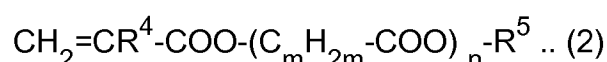
[0011]



[0012][In general formula (I), an alkyl group of the carbon numbers 1-5 or a phenyl group, and t of a hydrogen atom or an alkyl group of the carbon numbers 1-5, and  $\text{R}^3$  are repetition numbers, and  $\text{R}^1$  and  $\text{R}^2$  are the integers of 1-25, respectively. ]

[0013]\*\* Polar monomer 3 : it is a polar monomer expressed with a following general formula (2).

[0014]



[0015][In a general formula (2), an alkyl group of the carbon numbers 1-10 or a phenyl group, and n and m are repetition numbers, and an alkyl group of the carbon numbers 1-5 and  $\text{R}^5$  of  $\text{R}^4$  are the integers of 1-20, respectively. ]

[0016]In constituting a block copolymer constituent of this invention, it is preferred that the segment B contains a styrene system compound as the main ingredients. Thus, if a styrene system compound is contained, a mechanical strength of a block copolymer constituent can be raised more.

[0017]In constituting a block copolymer constituent of this invention, it is preferred to make a wt. ratio (segment A / segment B) of the segment A and the segment B into a value of 20 to 90 % of the weight / 10 to 80% of the weight of within the limits. If constituted in this way, compatibility over a mechanical strength and an ester compound of a block copolymer constituent, etc. can be demonstrated with sufficient balance.

[0018]what a polystyrene conversion average molecular weight (Mn) of block copolymer is made into a value of 5, 000-5, 000, and 000 within the limits for in constituting a block copolymer constituent of this invention -- things are preferred. If constituted in this way, compatibility over a mechanical strength and an ester compound of a block copolymer constituent, etc. can be demonstrated with sufficient balance, and it will become still easier [ manufacture of a block copolymer constituent or handling ].

[0019]In constituting a block copolymer constituent of this invention, it is preferred to make content of an ester compound into a value of 10-1, and 000 weight sections within the limits to block copolymer 100 weight section. If constituted in this way, compatibility over a mechanical strength and an ester compound of a block copolymer constituent, etc. can be demonstrated

with more sufficient balance.

[0020]

[Embodiment of the Invention] Hereafter, the embodiment in the block copolymer constituent of this invention is described concretely. First, a 1st embodiment of this invention, (1) Make into a constituent at least one polar monomer chosen from the group which consists of the polar monomer 1, the polar monomer 2, and the polar monomer 3. The block copolymer (the 1st ingredient may be called.) which consists of the segment B which carries out specific amount content by making into a constituent the segment A which carries out specific amount content, and the polar monomer concerned, (2) It is a block copolymer constituent containing an ester compound (the 2nd ingredient may be called.).

[0021] 1. The block copolymer which is the 1st ingredient in the block copolymer constituent of block copolymer this invention is constituted including the segment A and the segment B, as mentioned above.

[0022] (1) Contain the segment A segment A in order to raise compatibility with an ester compound. Therefore, at least one polar monomer is included as a constituent among the polar monomers 1-3 as shown below. The polar monomer concerned is restricted 10-100-mol% of within the limits. That is, the compatibility of block copolymer and an ester compound can be remarkably raised by being a specific amount, with containing a polar monomer specific in this way.

[0023] \*\* Polar monomer 1 : it is a polar monomer which has at least one sort of functional groups chosen from the group which becomes at least one polymerization nature unsaturated bond from a hydroxy group, a nitrile group, a carboxyl group, an amino group, and an amide group.

[0024] Concretely as a desirable example of the polar monomer which has a hydroxy group in the polar monomer 1, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, One sort, such as ethylene glycol mono- (meta) acrylate, mono- (meta) acrylate of polyalkylene glycol (2-12 repeating unit of alkylene glycol), and hydroxystyrene, or two sorts or more are mentioned. These polar monomers can be arbitrarily chosen according to the purpose of use.

[0025] As a desirable example of the polar monomer which has a nitrile group in the polar monomer 1, Acrylonitrile, a methacrylonitrile, alpha-ethylacrylonitrile, Methyl alpha-isopropylacrylonitrile, methyl alpha-n-butylacrylonitrile, 2-cyanoethyl (meta) acrylate, 2-(2-cyanoethoxy) ethyl alcohol and 3-(2-cyanoethoxy) propyl alcohol, 4 1 (2-cyanoethoxy) butyl alcohol, and 2 - [One sort, such as acrylate (meta) of 2-(2-cyanoethoxy) ethoxy] ethyl alcohol, or two sorts or more are mentioned. These polar monomers can be arbitrarily chosen according to the purpose of use.

[0026] As a desirable example of the carboxyl group content polar monomer in the polar monomer 1, One sort of the half ester of dicarboxylic acid, such as acrylic acid, methacrylic

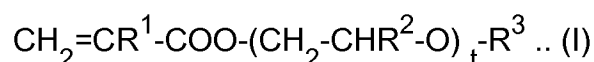
acid, maleic acid, fumaric acid, itaconic acid, tetra contest acid and succinic acid, or fumaric acid, and the unsaturated alcohol which has a polymerization nature group (reactant group), or two sorts or more are mentioned. These polar monomers can be arbitrarily chosen according to the purpose of use.

[0027]As a desirable example of the amino group content polar monomer in the polar monomer 1, (Meta) Acrylic acid dimethyl aminomethyl, acrylic acid (meta) dimethylaminoethyl, (Meta) An acrylic acid dimethylamino pro building, acrylic acid (meta) diethyl aminomethyl, (Meta) Diethylaminoethyl acrylate, acrylic (meta) \*\* diethylamino propyl, Dimethyl aminomethyl (meta) acrylamide, dimethylaminoethyl (meta) acrylamide, One sort, such as dimethylaminopropyl(meta) acrylamide, diethyl aminomethyl (meta) acrylamide, diethylaminoethyl (meta) acrylamide, diethylamino propyl(meta) acrylamide, and vinylpyridine, or two sorts or more are mentioned. These polar monomers can be arbitrarily chosen according to the purpose of use.

[0028]As a desirable example of the amide group content polar monomer in the polar monomer 1, Dimethyl(meta) acrylamide, diethyl(meta) acrylamide, Isopropyl(meta) acrylamide, acryloyl morpholine (meta), Dimethyl aminomethyl (meta) acrylamide, dimethylaminoethyl (meta) acrylamide, One sort, such as dimethylaminopropyl(meta) acrylamide, diethyl aminomethyl (meta) acrylamide, diethylaminoethyl (meta) acrylamide, and diethylamino propyl (meta) acrylamide, or two sorts or more are mentioned. These polar monomers can be arbitrarily chosen according to the purpose of use.

[0029]\*\* Polar monomer 2 : it is a polar monomer expressed with a following general formula (1).

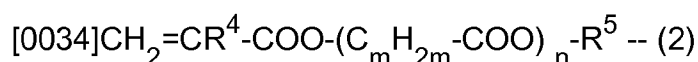
[0030]



[0031][In general formula (I), the alkyl group of the carbon numbers 1-5 or a phenyl group, and t of a hydrogen atom or the alkyl group of the carbon numbers 1-5, and  $\text{R}^3$  are repetition numbers, and  $\text{R}^1$  and  $\text{R}^2$  are the integers of 1-25, respectively. ]

[0032]As a desirable polar monomer expressed with a general formula (1), concretely, 2-methoxy ethyl (meta) acrylate, 2-ethoxyethyl (meta) acrylate, 2-methoxy propyl (meta) acrylate, 2-ethoxypropyl (meta) acrylate, 3-methoxy propyl (meta) acrylate, 3-ethoxypropyl (meta) acrylate, Methoxy polyethylene-glycol (the numbers of unit of ethylene glycol are 2-25) (meta) acrylate, Ethoxypolyethylene-glycol (meta) acrylate, phenoxypolyethylene-glycol (meta) acrylate, One sort, such as methoxy polypropylene-glycol (the numbers of unit of propylene glycol are 2-25) (meta) acrylate, ethoxypolypropylene-glycol (meta) acrylate, and phenoxypolypropylene-glycol (meta) acrylate, or two sorts or more are mentioned. These polar monomers can be arbitrarily chosen according to the purpose of use.

[0033]\*\* Polar monomer 3 : it is a polar monomer expressed with a following general formula (2).



[0035][In a general formula (2), the alkyl group of the carbon numbers 1-10 or a phenyl group, and n and m are repetition numbers, and the alkyl group of the carbon numbers 1-5 and  $\text{R}^5$  of  $\text{R}^4$  are the integers of 1-20, respectively. ]

[0036]As a desirable polar monomer expressed with a general formula (2), concretely,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_3\text{H}_6\text{COO}-\text{H}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_3\text{H}_6\text{COO}-\text{H}$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_4\text{H}_8\text{COO}-\text{H}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_4\text{H}_8\text{COO}-\text{H}$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{H}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{H}$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_3\text{H}_6\text{COO}-\text{CH}_3$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_3\text{H}_6\text{COO}-\text{CH}_3$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_4\text{H}_8\text{COO}-\text{CH}_3$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_4\text{H}_8\text{COO}-\text{CH}_3$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{CH}_3$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{CH}_3$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_3\text{H}_6\text{COO}-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_3\text{H}_6\text{COO}-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_4\text{H}_8\text{COO}-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_4\text{H}_8\text{COO}-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{C}_2\text{H}_5$  and  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{C}_4\text{H}_9$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{C}_4\text{H}_9$ ,  $\text{CH}_2=\text{CH}-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{C}_8\text{H}_{17}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{C}_5\text{H}_{10}\text{COO}-\text{C}_8\text{H}_{17}$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_3\text{H}_6\text{COO})_2-\text{H}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_3\text{H}_6\text{COO})_2-\text{H}$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_4\text{H}_8\text{COO})_2-\text{H}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_4\text{H}_8\text{COO})_2-\text{H}$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_2-\text{H}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_2-\text{H}$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_3\text{H}_6\text{COO})_2-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_3\text{H}_6\text{COO})_2-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_4\text{H}_8\text{COO})_2-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_4\text{H}_8\text{COO})_2-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_2-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_2-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_3-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_3-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_4-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_4-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_5-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_5-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_5-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_5-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_5-\text{C}_2\text{H}_5$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_2-\text{C}_8\text{H}_{17}$ , One sort, such as  $\text{CH}_2=\text{CH}-\text{COO}-(\text{C}_5\text{H}_{10}\text{COO})_2-\text{C}_8\text{H}_{17}$ , or two sorts or more are mentioned. These polar monomers can be arbitrarily chosen according to the purpose of use.

[0037]Next, the content of the polar monomer in the segment A mentioned above is explained. In this invention, it is making content of the polar monomer concerned into 10-100-mol% of value within the limits, and considering it as 20-100-mol% of value within the limits more

preferably. It is for a possibility that compatibility with the ester compound which the polarity of the segment A becomes low less than [ 10 mol % ], and the content of the polar monomer concerned swells may fall, and the swelling rate by an ester compound may fall to arise.

[0038]Although constituents in particular other than the polar monomer 1 in the segment A mentioned above - 3 are not limited, it is preferred to, use polymerization nature monomers, such as acrylate (meta), a conjugated diene compound, and a vinyl aromatic compound, for example.

[0039]Concretely as desirable (meta) acrylate, Methyl (meta) acrylate, ethyl (meta) acrylate, n-butyl (meta) acrylate, t One sort, such as KISHIRU (meta) acrylate, lauryl (meta) acrylate, and stearyl (meta) acrylate, or two sorts or more are mentioned to e rt-butyl (meta) acrylate and 2-ethyl. When methyl (meta) acrylate, ethyl (meta) acrylate, and n-butyl (meta) acrylate are used especially, compatibility with an ester compound improves more and the degree of swelling to block copolymer is preferred at the point which becomes large.

[0040]Concretely as a desirable conjugated diene compound, For example, 1, 3 1 butadiene, isoprene, 2, the 3-dimethyl 1, 3-butadiene, One sort, such as 1, 3-pentadiene, the 2-methyl 1, 3-pentadiene, 1, 3 1 hexadiene, 4, the 5-diethyl 1, 3-octadien, the 3-butyl- 1, 3-octadien, and chloroprene, or two sorts or more are mentioned. Industrial-utilizations nature is still higher, it is more preferred to use 1, 3 1 butadiene, isoprene, 1, and 3-pentadiene, in order to obtain polymer superior to that of physical properties, and it is using 1 and 3 1 butadiene and isoprene the optimal.

[0041]Concretely as a desirable vinyl aromatic compound, For example, one sort, such as styrene, alpha-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-tert-butylstyrene, o 1 methoxy styrene, m-methoxy styrene, and p-methoxy styrene, or two sorts or more are mentioned. It is preferred to use styrene, alpha-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, and p-tert-butylstyrene especially, in order industrial-utilizations nature is high and to obtain polymer superior to that of physical properties.

[0042](2) The segment B segment B formed the domain as a point in block copolymer constructing [ physical ] a bridge, and has achieved the function which raises the mechanical strength of the block copolymer concerned. Therefore, it is necessary to make into the value below 10 mol % the 1st mentioned above - the content of the 3rd polar monomer in the segment B concerned. This reason is because there is a possibility that the mechanical strength of a block copolymer constituent may fall, when the content of a polar monomer becomes more than 10 mol %. It is because the compatibility of an ester compound will become large not only to the segment A but to the segment B and the whole block copolymer will be plasticized more by details with an ester compound, if the content of the polar monomer in the segment B becomes more than 10 mol %. Therefore, it is making content of the polar monomer in the segment B into less than [ 5 mol % ] more preferably.

[0043]Although not limited in particular for constituents other than the polar monomer 1 in the segment B - 3, it is preferred to use polymerization nature monomers, such as same ingredient (meta), for example, acrylate, a conjugated diene compound, and a vinyl aromatic compound, also in the segment A.

[0044]Concretely as desirable (meta) acrylate, Methyl (meta) acrylate, ethyl (meta) acrylate, n-butyl (meta) acrylate, One sort, such as KISHIRU (meta) acrylate, lauryl (meta) acrylate, and stearyl (meta) acrylate, or two sorts or more are mentioned to tert-butyl (meta) acrylate and 2-ethyl.

[0045]Concretely as a desirable conjugated diene compound, For example, 1, 3 1 butadiene, isoprene, 2, the 3-dimethyl 1, 3-butadiene, One sort, such as 1, 3-pentadiene, the 2-methyl 1, 3-pentadiene, 1, 3 1 hexadiene, 4, the 5-diethyl 1, 3-octadien, the 3-butyl- 1, 3-octadien, and chloroprene, or two sorts or more are mentioned.

[0046]Concretely as a desirable vinyl aromatic compound, For example, one sort, such as styrene, alpha-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-tert-butylstyrene, o 1 methoxy styrene, m-methoxy styrene, and p-methoxy styrene, or two sorts or more are mentioned. It is preferred to use styrene, alpha-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, and p-tert-butylstyrene from a viewpoint from which especially the shape retentivity of the constituent after swelling an ester compound is excellent, and a higher mechanical property is acquired.

[0047](3) Explain the integrated state of the segment A and the segment B, next the integrated state of the segment A and the segment B. Although the integrated state in particular of the segment A concerned and the segment B is not limited, For example, At least one sort of polar monomers chosen from the polar monomers 1-3 are made into a constituent. 10-100-mol % -- it is preferred that the content of the segment A (it is written as A.) to contain and a polar monomer is the (A)-(B) block copolymer with which the segment B (it is written as B.) which is less than [ 10 mol % ] was combined. The (B)-(A)-(C) block copolymer which consists of a taper block segment (it is written as C.) in which the content of the polar monomers 1-3 decreases gradually is also preferred at segment A (A), and a segment (B) and within the limits below 10 mol %. It is desirable even if it is the (B)-(A)-(B) block copolymer etc. which consist of segment B (B), and segment A (A) and segment B (B) in this order.

[0048]Above-mentioned (A)-(B) block copolymer, (B)-(A)-(C) block copolymer, Considering it as the block copolymer which extended or branched also has a preferred segment which is expressed with following general formula (3) - (5) via the residue of a coupling agent, respectively in (B)-(A)-(B) block copolymer.

[0049]

$[(B)-(A)]_p-X$  (3)

[0050]In [general formula (3)], p shows the integer of 2-4 and X shows the residue of a cup



RINNGU agent. ]

[0051]

$[(B)-(A)-(C)]_p-X$  (4)

[0052]In [general formula (4), p shows the integer of 2-4 and X shows the residue of a cup RINNGU agent. ]

[0053]

$[(B)-(A)-(B)]_p-X$  (5)

[0054]In [general formula (5), p shows the integer of 2-4 and X shows the residue of a cup RINNGU agent. ]

[0055](4) Explain the ratio of the segment A and the segment B, next the ratio of the segment A in block copolymer, and the segment B. Although not limited in particular for the ratio of the segment A concerned and the segment B, when weight of the whole block copolymer is made into 100 % of the weight, It is considering it as the value of 30 to 85% of the weight of within the limits preferably [ making weight of the segment A into the value of 20 to 90% of the weight of within the limits ], and more preferably. When the weight of the segment A will be less than 20 % of the weight, it is because there is a possibility that the compatibility of the block copolymer to an ester compound may fall and the degree of swelling in a block copolymer constituent may become small as a result. Therefore, when long term storage of the block copolymer constituent is carried out, there is a possibility that an ester compound may ooze out. It is because there is a possibility that the weight of the segment B may decrease relatively, the mechanical strength of a block copolymer constituent may fall, and shape retentivity may fall if the weight of the segment A exceeds 90 % of the weight, on the other hand.

[0056]When weight of the whole block copolymer is made into 100 % of the weight also with the weight of the segment B, it is considering it as the value of 25 to 70% of the weight of within the limits preferably [ considering it as the value of 10 to 80% of the weight of within the limits ], and more preferably. When the weight of the segment B will be less than 10 % of the weight, it is because there is a possibility that the mechanical strength of a block copolymer constituent may fall and shape retentivity may fall. On the other hand, when the weight concerned exceeds 80 % of the weight, it is because there is a possibility that the weight of the segment A may decrease relatively and the compatibility of the block copolymer to an ester compound may become low.

[0057]The compatibility over the mechanical strength and ester compound of a block copolymer constituent, etc. can be demonstrated with sufficient balance by constituting the ratio of the segment A and the segment B in this way as above.

[0058](5) Explain a molecular weight, next the polystyrene conversion number average molecular weight (it only carries out abbreviated to a molecular weight or Mn hereafter.) of

block copolymer. It is preferred to make the polystyrene conversion number average molecular weight (henceforth [Mn]) of the block copolymer concerned into the value of 5,000-5,000, and 000 within the limits. When the molecular weight of block copolymer became 5 or less than 000 value and it adds an ester compound to the block copolymer concerned, it is because there is a possibility that the shape retentivity of a block copolymer constituent may fall. It is because there is a possibility that the processability of the spare time which processes the block copolymer concerned may get worse, or compatibility with an ester compound may fall, on the other hand when the molecular weight of block copolymer exceeds 5,000, and 000. [0059]Therefore, the shape retentivity of a block copolymer constituent and balance with processability etc. the molecular weight of block copolymer from a better viewpoint more preferably, It is considering it as the value of 7,000-2,000, and 000 within the limits, and is considering it as the value of 10,000-1,000, and 000 within the limits the optimal. The molecular weight of block copolymer measures the elution time of the block copolymer from a column using a GPC (gel permeation chromatography) device, and The elution time concerned, It can ask by contrasting the analytical curve (elution time and molecular weight) beforehand prepared in standard polystyrene.

[0060](6) Explain a manufacturing method, next the manufacturing method of block copolymer. Although the manufacturing method in particular of the block copolymer concerned is not limited, it can take the method shown in (b) - (\*\*) below, for example.

[0061](b) How to compound another side succeedingly and to manufacture block copolymer after compounding either the segment A or the segment B.

(\*\*) How to combine each and to manufacture block copolymer by a coupling reaction after compounding the segment A and the segment B independently.

(\*\*) How to compound the segment B using the polymerization initiator which has segment A structure, and to manufacture block copolymer in a molecule.

(\*\*) How to compound the segment A using the polymerization initiator which has segment B structure, and to manufacture block copolymer in a molecule.

[0062]Control of a block structure and the molecular weight control in each segment are easier, After compounding either the segment A or the segment B from the point that it is possible to compound block copolymer with one reaction vessel, the method of the above-mentioned (b) which is the method of compounding another side succeedingly is more preferred. In order to enforce the method of this (b), more specifically, it is preferred to adopt living anionic polymerization, living cationic polymerization, living radical polymerization, etc.

[0063]Since the block copolymer used for the block copolymer lot product of this invention is manufactured by polymerizing a functional group content monomer or a polar monomer, as a manufacturing method, its living radical polymerization which is not influenced by these functional groups is still more preferred.

[0064]And the atomic move living-radical-polymerization method using organic halogenated compound, copper halide and 2, and 2-pyridine as living radical polymerization, It can illustrate as a more desirable manufacturing method (J. Am.Chem. Soc., 114, 5614 (1995) and Macromolecules, 28, 7901 (1995) references).

[0065]2. The block copolymer constituent of ester compound this invention is constituted including the ester compound (an ester system compound may be called in a broad sense.) whose number is the 2nd.

[0066]Here, although not limited especially as an ester compound of the 2nd ingredient, at the service temperature (25 \*\* as an example) from a user-friendly viewpoint, a liquefied thing is preferred.

[0067]As a kind of desirable ester compound, For example, methyl acetate, ethyl acetate, isopropyl acetate, Acetate, such as n 1 butyl acetate; Methylpropionate, ethyl propionate, Propionate, such as butyl propionate; Methylacetoacetate, Acetoacetates, such as ethylacetoacetate and tert-butylacetoacetate; Methyl (meta) acrylate, Ethyl (meta) acrylate, n-butyl (meta) acrylate, tert-butyl (meta) acrylate, To 2-ethyl, KISHIRU (meta) acrylate, n 1 octyl (meta) acrylate, Alkyl (meta) acrylate, such as lauryl (meta) acrylate; Crotonic acid methyl, Ethyl crotonate, crotonic acid n1 propyl, crotonic acid n-butyl, Unsaturation monocarboxylic acid ester species, such as \*\*\*\* leather acid ethyl, \*\*\*\* leather acid n-propyl, and \*\*\*\* leather acid n-butyl; Ethylene glycol, 1, 2-propanediol, the 3-chloro- 1, 2-propanediol, 1, 3-propanediol, 1, 2-butanediol, 1, 3-butanediol, 1, 4-butanediol, 1, 5-pentanediol, 1, Monod or di(meth) acrylate of alkylene glycol, such as 6-hexandiol; A polyethylene glycol, Monod or di(meth) acrylate of polyalkylene glycols (the alkylene KURIKORU numbers of unit are 2-25), such as a polypropylene glycol; 2-methoxy ethyl (meta) acrylate, 2-ethoxyethyl (meta) acrylate, 2-methoxy propyl (meta) acrylate, 2-ethoxypropyl (meta) acrylate, 3 1 methoxy propyl (meta) acrylate, Alkoxy alkyl (meta) acrylate, such as 3 1 ethoxypropyl (meta) acrylate; A methoxy polyethylene glycol, An ethoxypolyethylene glycol, a methoxy polypropylene glycol, The acrylate (meta) of alkoxy polyalkylene glycols (the alkylene glycol numbers of unit are 2-25), such as an ethoxypolypropylene glycol; 2-phenoxyethyl (meta) acrylate, Aryloxy alkyl (meta) acrylate, such as 2-phenoxypropyl (meta) acrylate and 3-phenoxypropyl (meta) acrylate; A phenoxypolyethylene glycol, The mono- (meta) acrylate of aryloxy polyalkylene glycols (the alkylene glycol numbers of unit are 2-25), such as a phenoxypolypropylene glycol; 2-cyanoethyl (meta) acrylate, Cyano alkyl (meta) acrylate, such as 3-cyanopropyl (meta) acrylate; 2-(2-cyanoethoxy) ethyl alcohol, 3-(2-cyanoethoxy) propyl alcohol, 4 1 (2 1 cyanoethoxy) butyl alcohol, Cyanoalkoxy alkyl (meta) acrylate, such as 2-[2-(2-cyanoethoxy) ethoxy] ethyl alcohol; Glycerin, 1, 2, 4-butanetriol, pentaerythritol, a TORIMECHI roll alkane (the carbon numbers of an alkane are 1-3), mono- of polyhydric alcohol more than trivalent, such as a tetramethylolalkane (the carbon numbers of an alkane are 1-3), or oligo (meta-)

acrylate; -- polyhydric alcohol more than trivalent [ said ], Mono- [ of a polyalkylene glycol addition ], or oligo (meta) acrylate; 1, 4-cyclo hexanediol, 1, 4-benzenediol, 1, Mono- or oligo (meta) acrylate of cyclic diol, such as 4-dihydroxyethylbenzene; Ethylene carbonate, Dimethyl carbonate, methylethyl carbonate, methylpropyl carbonate, Methylisopropyl carbonate, diethyl carbonate, ethylpropyl carbonate, Ethylisopropyl carbonate, propylene carbonate, dipropyl carbonate, Lactone, such as carbonate; beta-butyrolactones, such as diisopropyl carbonate and butylene carbonate, gamma-butyrolactone, gamma-caprolactone, and epsilon-caprolactone, is mentioned. These ester compounds are possible also for using it alone, or can also mix and use two or more sorts.

[0068] It is preferred to make into the value of ten to 1000 weight section within the limits the ratio (addition) of the ester compound in the block copolymer constituent of this invention mentioned above to block copolymer 100 \*\*\*\*\* as the 1st ingredient. When there is a possibility that the characteristic (EFFECT OF THE INVENTION) of the ester compound in a block copolymer constituent may not fully be obtained when the ratio of an ester compound is less than ten weight sections and 1000 weight sections are exceeded on the other hand, it is because there is a possibility that the mechanical strength of a block copolymer constituent may fall remarkably.

[0069] Therefore, it is more preferred that the balance of the mechanical strength in the addition effect and block copolymer constituent of an ester compound makes the ratio (addition) of an ester compound the value of 20 to 700 weight section within the limits from a better viewpoint to block copolymer 100 \*\*\*\*\*.

[0070] 3. The block copolymer constituent of other addition ingredient this inventions can add the third component shown below in addition to the 1st ingredient mentioned above and the 2nd ingredient.

[0071] (1) Addition combination of a heat radical generator or the optical radical generator can be carried out in order to give the characteristic according to a use to the block copolymer constituent of radical generator this invention. Namely, for example, when acrylate is used in some numbers (meta) as an ester compound. By blending a generating agent and an optical radical generator, it becomes possible to use it as a block copolymer constituent of the thermosetting which can construct a bridge by heat or lights (ultraviolet rays, visible light, etc.), or a photoresist.

[0072] As a desirable heat radical generator, for example as organic peroxide, the 1,1-di-tert-butylperoxy 3 and 3, 5-trimethylcyclohexane, Di-tert-butyl peroxide, tert-butyl cumyl peroxide, Di-cumyl peroxide, 2,5-di-methyl-2,5-JI (tert-butylperoxy) hexane, 2,5-di-methyl-2,5-JI (tert-butylperoxy) hexyne, 1, 3 bis-(tert-butylperoxy \*\*\*\*- propyl) benzene, tert-butylperoxy \*\*\*\*-propyl carbonate, acetylcyclohexylsulfonyl peroxide, \*\*\*\*- butyl peroxide, di-isopropyl peroxi dicarbonate, Di-allyl peroxi dicarbonate, di-n-propyl peroxi dicarbonate, Di-(2-ethoxyethyl)

peroxi dicarbonate, JI (methoxy isopropyl) peroxi dicarbonate, Di(2-ethylhexyl) peroxi dicarbonate, tert-hexyl peroxy neo HEKISANETO, JI (3-methyl-3-MECHIROKISHI butyl) peroxi dicarbonate, tert-butylperoxy neodecanate, tert-hexyl peroxy neodecanate, tert-butylperoxy neo hexa NETO, 2, 4-dichlorobenzoyl peroxide, A tert-hexyl perky SHIPIBA rate, the tert-butyl par HEKISHI pivalate, 3, 3, 5-trimethylhexanoyl peroxide, octanoyl peroxide, Decanoyl peroxide, lauroyl peroxide, cumyl peroxy OKUTETO, Acetyl peroxide, tert-butylperoxy (2-ethyl hexanate), Benzoyl peroxide, tert-butylperoxy isoiso butyrate, 1,1-bis(tert-butylperoxy) cyclohexane, tert-butylperoxy MAREIKKU acid, tert-butylperoxy laurate, tert-butylperoxy 3,3,5-trimethyl hexa NETO, Cyclohexanon peroxide, tert-butylperoxy allyl carbonate, 2,5-dimethyl-2,5-JI (benzoylperoxy) hexane, 2,2-bis(tert-butylperoxy)octane, tert-butylperoxy acetate, 2,2-bis(tert-butylperoxy)butane, tert-butylperoxy benzoate, n-butyl-4,4-bis(tert-butylperoxy) valerate, Di-tert-butyl JIPA oxy isophthalate, methyl ethyl ketone peroxide, alpha and alpha'-bis (tert-butylperoxy m-isopropyl)hexane, Di-isopropyl benzene hydronalium peroxide, p-methanehydronalium peroxide, 1,1,3,3-tetramethylbutyl hydroperoxide, 2,5, and - dimethylhexane 2,5-dihydroperoxide, cumene hydronalium peroxide, tert-butylhydronalium peroxide, etc. can be mentioned. These can also use a kind alone, and can also mix and use two or more sorts. It is also desirable to use a polyfunctional unsaturated compound etc. together to organic peroxide as a bridge construction auxiliary agent.

[0073]. As a desirable optical radical generator, are usually used as a photosensitizer. For example, alpha-diketone compounds, such as a JIASHI roil and benzyl; Benzoin, Acyloins, such as PIBAROIN; Benzoin methyl ether, benzoin ethyl ether, Acyloin ether, such as benzoin propyl ether; benzophenones, such as polynuclear quinone;2, such as anthraquinone, 1, and 4-naphthoquinone, 2-dimethoxyphenylacetophenone, and methyl-o-benzoyl benzoate, are mentioned. These can also use a kind alone, and can mix and use two or more sorts.

[0074](2) When using it as a block copolymer constituent of polymerization inhibitor and the thermosetting mentioned above, or a photoresist, polymerization inhibitor may be blended in the range which does not spoil the effect of this invention. By using polymerization inhibitor, thermosetting or a photoresist can be controlled easily and the preservation stability of a block copolymer constituent can be raised remarkably.

[0075]As desirable polymerization inhibitor, hydroquinone, hydroquinone monomethyl ether, Mono-t1 butylhydroquinone, catechol, p-methoxy phenol, p-tert-butylcatechol, 2, 6-di-tert 1 butyl-p-cresol, Quinone, such as 2, 8-di-tert-butyl-m-cresol, pyrogallol, and beta-naphthol; Nitrobenzene, m-dinitrobenzene, 2-methyl-2-nitrosopropane, alpha 1 phenyl-tert-butylNitron, A nitro compound or nitron compounds, such as 5 and 5 1 dimethyl- 1-pyrroline 1 1 oxide; A chloranil amine system, Diphenylamine, diphenyl picryl hydrazine, phenol alpha-naphthylamine, Amines, such as pyridine and phenothiazin; A dithiobenzoylsulfide, Sulfides;1, such as dibenzyltetrasulfide, 1-diphenylethylene, Unsaturated compounds, such as alpha-

methylthio acrylonitrile; Thiazine dye; 1, such as thionine blue, toluidine-blue, and methylene blue, and 1-diphenyl-2-picrylhydrazyl, 1 and 3, 5 1 triphenyl Felder Jill, the 4-hydroxy- 2, 2, and 6, Stable radicals, such as KISAJI en- 1-ylidene- p-trio KISHIRU, etc. can be mentioned to 6-tetramethylpiperidine 1-oxyl, 2, the 6 1 di-tert-butyl-alpha-(3, 5-di-tert-butyl)14-oxo 2, and 5 1 cyclo. These polymerization inhibitor can also be used alone, or can also mix and use two or more sorts.

#### [0076](3) Electrolyte (salt)

To use the block copolymer constituent of this invention as a solid electrolyte in electrochemical devices, such as a lithium secondary battery, it is necessary to add an electrolyte (salt). Although the electrolyte concerned changes with uses of the solid electrolyte to manufacture, For example, when the application to a lithium secondary battery is taken into consideration, as a desirable electrolyte,  $\text{LiClO}_4$ ,  $\text{LiAlCl}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_4$ ,  $\text{LiNbF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSCN}$ ,  $\text{LiCl}$ ,  $\text{Li}(\text{CF}_3\text{SO}_3)$ ,  $\text{Li}(\text{C}_4\text{F}_9\text{SO}_3)$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ,  $\text{LiI}$ ,  $\text{LiCl}$ , Lithium salt of  $\text{Li}(\text{C}_6\text{H}_5\text{SO}_3)$ ; alkali metal salt, alkaline earth metal salt, etc., such as  $\text{NaBF}_4$ , ammonium benzoate, or ammonium tartrate, can be mentioned. These electrolytes can also be used alone, or can also mix and use two or more sorts.

[0077]It is preferred to make concentration at the time of dissolving an electrolyte in a solvent into the value of 0.001 - 5 mol/L within the limits. When the concentration of the electrolyte concerned becomes the outside of this range, it is for a possibility that the charging and discharging characteristic in an electrochemical device may fall to arise.

[0078]4. Explain a manufacturing method, next the manufacturing method of the block copolymer constituent in this invention. Although the manufacturing method in particular of the block copolymer constituent concerned is not restricted, the following manufacturing methods can be used for it, for example.

[0079](1) Fully carry out agitation mixing of the additive agent etc. the 1st ingredient (block copolymer), the 2nd ingredient (ester system compound), and if needed using NI 1 DA, INTAMIKISA, etc., and manufacture a block copolymer constituent.

(2) Manufacture a block copolymer constituent by fully fabricating an additive agent etc. after agitation mixing the 1st ingredient (block copolymer) and if needed using NI 1 DA, INTAMIKISA, etc., and adding the 2nd ingredient (ester system compound) after that.

[0080](3) Carry out the cast on a substrate after dissolving an additive agent in an organic solvent the 1st ingredient (block copolymer) and if needed, pressure reduction operation etc. remove an organic solvent, and it is cast film \*\*\*\*. Subsequently, a block copolymer constituent is manufactured by immersing this cast film in the 2nd ingredient (ester system compound) ingredient (2) which mixed the additive agent the 2nd ingredient (ester system compound) or if needed.

(4) When acrylate is used in some numbers (meta) as an ester compound, blend a generating agent and an optical radical generator further, rank second and manufacture the block copolymer constituent which constructed the bridge by irradiating with heating or light.

[0081]

[Example] Hereafter, an example explains this invention still in detail. However, it is only explaining this invention generally and the following explanation is not limited in particular to the groundless statement of the following [ this invention ].

[0082] In the following explanation, n-butyl acrylate and HEA show 2-hydroxyethyl acrylate, EDEA shows ethoxydiethylene-glycol acrylate, and, as for ST as a kind of monomer, AN shows acrylonitrile, respectively, as for styrene and BA. EGMA as an ester compound shows ethylene glycol dimethacrylate, PC shows propylene carbonate, and gamma-BL shows gamma-butyrolactone, respectively. Mn showed the number average molecular weight of polystyrene conversion, and Mw showed the weight average molecular weight of polystyrene conversion, and measured it using gel PAMIESHON chromatography (GPC is called hereafter.), respectively. A "weight section" is meant unless a "part" has a notice in particular in the following explanation.

[0083] [The synthetic example 1]

(Composition of the segment A) The nitrogen purge of the 1000-ml separable flask provided with the flowing-back condenser tube, the thermometer, the nitrogen introducing pipe, and the agitator is carried out, 2.8 g of copper bromide (I)sg [ 3.06 ] and 2, 9.96 g of 2-bipyridines, alpha, and alpha' 1 dibromo p1 xylene, the diphenyl ether 200g, and EDEA200g were accommodated in this, respectively. And the separable flask in which these reaction mixtures were accommodated under the nitrogen air current while agitating was heated at 90 \*\* using the oil bath, and EDEA as a monomer was polymerized.

[0084] The reaction mixture which contains EDEA in the middle of a polymerization was sampled suitably, this was diluted with the tetrahydrofuran, and the diluent was created. And in accordance with the conventional method, the amount of consumption of EDEA (monomer) was measured for this diluent using gas chromatography (GC is called hereafter.), and polymerization conversion was computed. And when the polymerization conversion of EDEA reached to 93%, the separable flask was cooled and the polymerization of the segment A was ended. Mn is 14,000 when the molecular weight of the obtained segment A is measured using GPC.

Mw/Mn used as the rule of thumb of molecular weight distribution was 1.3.

[0085] (Composition of block polymer) ST200g was further added to the separable flask in which the above-mentioned reaction mixture was accommodated as a segment B ingredient, and it added, and heated at the temperature of 90 \*\* succeedingly, and EDEA which remains

as a polymerization and monomer of ST was polymerized. And when the polymerization conversion of ST reached to 63% 97%, the polymerization conversion of EDEA cooled the separable flask in which the reaction mixture was accommodated, and ended the polymerization. Subsequently, the reaction mixture was poured out into n-hexane, reduced pressure drying of the produced precipitation was filtered and carried out, and block polymer (P-1) was obtained.

[0086]Mn is 23,000 when the molecular weight of P-obtained 1 is measured using GPC. Mw/Mn was 1.5.

Since the molecular weight is increasing from the segment A with monophasicity [ molecular weight distribution ] (even [ peak ]), block polymerization advances and it is presumed that triblock polymer of the segment B-segment A-segment B is obtained. The monomer composition of the amount of consumption of each monomer determined by GC to the segment B is ST/EDEA=96/4 (mol%).

The ratio of the segment A and the segment B obtained the result of A/B=58 / 42 (wt%).

The presentation and molecular weight (Mn, Mw/Mn) of block copolymer which were obtained are shown in Table 1, respectively.

[0087]

[Table 1]



合成例	合成例1	合成例2	合成例3	合成例4	合成例5	合成例6	合成例7
ポリマー(種類)	P-1	P-2	P-3	P-4	P-5	P-6	P-7
ポリマー構造	BAB7ブロック体	BAB7ブロック体	BAB7ブロック体	BAB7ブロック体	BAB7ブロック体	BAB7ブロック体	ランダム共重合体
セグメントA							
組成							
ST (mol%)							
BA (mol%)		79	55		71	97	
HEA (mol%)		21					
EDEA (mol%)	100		45	100			
AN (mol%)					29	3	
Mn	13,800	31,600	52,000	12,200	12,200	20,800	
Mw/Mn	1.3	1.5	1.4	1.3	1.3	1.5	
セグメントB							
組成							
ST (mol%)		85	89	70	100	100	
BA (mol%)		12	6				79
HEA (mol%)		3					21
EDEA (mol%)	4		5	30			
AN (mol%)							
セグメントC							
組成							
ST (mol%)							
BA (mol%)							
HEA (mol%)							
EDEA (mol%)							
AN (mol%)							
Mn	58/42	68/32	73/27	47/53	61/39	1	
Mw/Mn	23,200	46,300	73,100	25,800	29,500	43,200	72,000
	1.5	1.8	1.8	1.6	1.8	1.8	3.4

[0088][Synthetic examples 2-4] on the same procedure as the synthetic example 1, and conditions. Copolymerization (synthetic example 3 and preparation ratio % of 550/45 mol) of BA/HEA (synthetic example 2 and preparation ratio % of 790/21 mol) or BA/EDEA or homopolymerization (synthetic example 4 and preparation ratio % of 100 mol) of EDEA was

performed. The molecular weight ( $M_n$ ,  $M_w/M_n$ ) as the segment A obtained at this time was measured like the synthetic example 1. Each measurement result is shown in Table 1.

Subsequently, ST was added further, on the same procedure as the synthetic example 1, and conditions, block polymerization of the segment B was performed and block copolymer (P-2), (P-3), and (P-4) were obtained, respectively. The molecular weight of the obtained block copolymer was measured using GPC like the synthetic example 1, and composition ratio was further measured using GC. Each measurement result is shown in Table 1.

[0089][Synthetic examples 5-6] After polymerizing the segment A which consists of BA/AN (synthetic example 5) or ST/AN (synthetic example 6) on the same procedure as the synthetic example 1, and conditions, the vacuum pump was connected with the separable flask and decompression removal of the unreacted monomer was carried out. The molecular weight ( $M_n$ ,  $M_w/M_n$ ) as the segment A obtained at this time was measured like the synthetic example 1. Each measurement result is shown in Table 1. Subsequently, ST was added further, on the same procedure as the synthetic example 1, and conditions, block polymerization of the segment B was performed and block copolymer (P-5) and (P-6) were obtained. The molecular weight of the obtained block copolymer was measured like the synthetic example 1 using GPC, and composition ratio was further measured using GC. Each measurement result is shown in Table 1.

[0090][Synthetic example 7] The nitrogen purge of the 1000-ml separable flask provided with the flowing-back condenser tube, the thermometer, the nitrogen introducing pipe, and the agitator was carried out, and 0.38 g of azobisiso PUCHIRO nitril (azobisisobutyronitrile), 563 g of toluene, BA152.5g, and HEA34.5g were accommodated in this, respectively. And the separable flask in which these reaction mixtures were accommodated under the nitrogen air current while agitating was heated at 60 °C using the oil bath, and the polymerization of BA and HEA as a monomer was performed over 10 hours.

[0091]Subsequently, when the amount of consumption of the monomer was calculated using GC and the polymerization conversion of the monomer was computed, 90% of value was obtained. The monomer composition of the polymer calculated from the amount of consumption of the monomer was BA/HEA=79/21. n-hexane was filled with the obtained reaction mixture, the formed precipitate was filtered, it was pressure-dried and random KOBORIMA (P-7) was obtained. And  $M_n$  is 72,000 when a molecular weight is measured using GPC.

$M_w/M_n$  was 3.4.

[0092][Example 1] (creation of a block copolymer constituent)

The block copolymer (P-1) compounded in the synthetic example 1 was dissolved in toluene, and the polymer solution of concentration was prepared 10% of the weight. This polymer

solution was developed on the petri dish made from Teflon, and it dried by ordinary temperature and ordinary pressure for 8 hours. Then, further, under 30 \*\* and decompression, it was made to dry on the conditions of 10 hours, and the cast film was obtained. This cast film is immersed into gamma-BL as an ester compound for 24 hours, and was swollen, and the block copolymer constituent of this invention made into the purpose was obtained.

[0093](Evaluation of a block copolymer constituent)

By the method shown below, the degree of swelling in a block copolymer constituent, solution retention, and shape holding property were measured.

[0094](1) From the after-swelling weight after the cast film of degree-of-swelling block polymer in a block copolymer constituent is immersed into an ester compound for 24 hours, and the weight before swelling, the degree of swelling in a block copolymer constituent was computed using the lower type. A measurement result is shown in Table 2. degree of swelling (%) = --

[front [ after-swelling weight (g)-swelling ] weight (g)] / after-swelling weight (g) x100 [0095](2) The cast film which immersed into the solution retention ester compound in a block copolymer constituent for 24 hours was neglected in the glass petri dish, and the after-swelling weight after 10 more hour progress was measured. And the degree of swelling as solution retention was measured from the after-swelling weight before and behind 10-hour progress using the above-mentioned formula. A measurement result is shown in Table 2.

[0096](3) the shape retentivity in the block copolymer constituent from the appearance of the cast film which immersed into the shape retentivity ester compound in a block copolymer constituent for 24 hours -- the following decision criterion -- with, it judged. A decision result is shown in Table 2. If excelled in the shape retentivity concerned, it can be said that it excels also in the mechanical strength of a block copolymer constituent.

x: Dissolve into an ester compound and fixed shape maintenance is impossible.

\*\* : Although definite shape is held in an ester compound, plastic deformation will be carried out if it is made to elongate.

O: even if definite shape is held and it elongates in an ester compound, rubber elasticity is shown, and return to the original shape.

[0097]As easily understood from the result shown in Table 2, the block copolymer constituent of this invention shows not less than 87% of high degree of swelling, and is not less than 73% also about solution retention.

It was checked that shape holding property is also excellent.

[0098]

[Table 2]

実施例	実施例1	実施例2	実施例3	実施例4	比較例1	比較例2	比較例3
組	P-1	P-2	P-3	P-5	P-4	P-6	P-7
成	100	100	100	100	100	100	100
物	γ-BL	PC	EG	EG	γ-BL	EG	PC
	681	307	363	492	8	8	8
物	87.2	75.4	78.4	83.1	—	7.4	—
性	73.7	62.6	67.2	72.1	—	6.8	—
	○	○	○	○	×	○	×
膨潤度							
保液性(10時間後の膨潤度(%))							
形状保持性							

[0099][Examples 2-4] (creation of a block copolymer constituent)

The block copolymer constituent was created like Example 1 using the ester compound shown in Table 2. That is, in Example 2, block copolymer (P-2) and PC as an ester compound were used, and the block copolymer constituent was created. In Example 3, block copolymer (P-3) and EG as an ester compound were used, and the block copolymer constituent was created.

In Example 4, block copolymer (P-5) and EG as an ester compound were used, and the block copolymer constituent was created.

[0100](Evaluation of a block copolymer constituent) By the same method as Example 1, the degree of swelling in a block copolymer constituent, solution retention, and shape holding property were measured, respectively. A measurement result is shown in Table 2. Although the block copolymer constituent (examples 2-4) of this invention was changed a little according to the kind of ester compound to be used, it showed not less than 75% of high degree of swelling altogether, so that I might be easily understood from the result shown in Table 2. Not less than 62% of high value was altogether shown also about solution retention, and it was checked further that shape holding property is also excellent.

[0101][Comparative examples 1-3] (creation of a block copolymer constituent)

The block copolymer constituent was created like Example 1 using the ester compound shown in Table 2. That is, in the comparative example 1, block copolymer (P-4) and gamma-BL as an ester compound were used, and the block copolymer constituent was created. In the comparative example 2, block copolymer (P-6) and EG as an ester compound were used, and the block copolymer constituent was created. In the comparative example 3, block copolymer (P-7) and PC as an ester compound were used, and the block copolymer constituent was created.

[0102](Evaluation of a block copolymer constituent) By the same method as Example 1, the degree of swelling in a block copolymer constituent, solution retention, and shape holding property were measured, respectively. A measurement result is shown in Table 2. In the comparative example 1, the polymer dissolved in gamma-BL as an ester compound, it did not become a constituent of swelling nature, and definite shape was not able to be held from an initial stage so that I might be easily understood from the result shown in Table 2. Since there is too much amount of EDEA used in the segment B of polymer (P-4) as this reason, compatibility with gamma-BL as an ester compound becomes good, and it is presumed for the segment B itself dissolving in gamma-BL. About the comparative example 1, in order to show that the degree of swelling and solution retention in Table 2 were not able to be measured, (-) is indicated to the corresponding section.

[0103]Although considered because there is little content of AN in the segment A of polymer (P-6) in the comparative example 2, since it is lacking in compatibility with EG as an ester compound, it does not become a constituent with a big degree of swelling. In the comparative example 3, the random copolymer (P-7) dissolved in PC as an ester compound, it did not become a constituent of swelling nature, and definite shape was not able to be held from an initial stage. Therefore, about the comparative example 3, in order to show that the degree of swelling and solution retention in Table 2 were not able to be measured, (-) is indicated to the corresponding section.

[0104]

[Effect of the Invention]As explained above, the block copolymer lot product of this invention, The block copolymer lot product excellent in the balance of the degree of swelling etc. which were called conventionally opposite characteristic, a mechanical strength, etc. can be provided now by carrying out specific amount use of the specific polar monomer into the block copolymer 1. That is, the degree of swelling to an ester compound was large, and while excelling in solution retention, the block copolymer lot product excellent in a mechanical strength or shape retentivity could be provided.

[0105]Therefore, the block copolymer constituent of this invention can be used very conveniently as solid electrolyte materials adjusted by making it swell with the organic solvent in which metal salt was dissolved.

[0106]The block copolymer constituent of this invention produces block copolymer using the usual solution polymerization etc.

Then, manufacture of the solid electrolyte of the lithium secondary battery which it becomes unnecessary to have processed the conventional polar polymers under the elevated temperature, and uses the block copolymer constituent concerned from the ability to manufacture only by adding an ester compound, etc. became very easy.

[0107]It can be considered now as the constituent of thermosetting or a photoresist by using the ester compound which has a polymerization nature unsaturated bond, and a suitable polymerization initiator. Therefore, the constituent concerned can be widely used for a paint, adhesives, printed boards, or a molding material.

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[Translation done.]